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MWQI Summary and Findings from Data Collected August 1998 through September 2001 Chapter 2 Data Collection and Analysis - Content			

# **Chapter 2 Data Collection and Analysis**

#### **Selection of Constituents**

The following constituents are discussed in this order:

- Total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UVA<sub>254</sub>), formation potential of trihalomethanes (THMs) and haloacetic acids (HAAs).
- Bromide.
- Salinity including electrical conductivity (EC)—also referred to as specific conductance in older publications—total dissolved solids (TDS), chloride, sulfate, sodium, calcium, and magnesium.
- pH, alkalinity, hardness, and turbidity.
- Methyl tert-butyl ether (MTBE), aluminum, copper, iron, manganese, silver, and zinc.
- Antimony, arsenic, barium, cadmium, chromium, lead, mercury, nickel, and selenium.
- Ammonia, nitrate, nitrate and nitrite, Kjeldahl nitrogen, orthophosphorus, and total phosphorus.
- Boron.

Historical data and recent findings in *Sanitary Survey Update Report 2001* (DWR 2001) suggest that these constituents represent the major parameters of concern in Sacramento-San Joaquin Delta (the Delta) source waters. They directly affect the quality of finished drinking water processed from Delta source waters.

## **Sample Collection**

The Field Support unit of the Municipal Water Quality Program Branch under the Department's Office of Water Quality sampled at 12 of the 14 stations. The Division of Operations and Maintenance of the California Department of Water Resources (DWR) collected samples at the Banks and Delta-Mendota Canal stations. Because samples from all stations cannot be collected within one day due to distances between stations and limitations in resources, the samples were collected on 3 different one-day sampling runs within one week with each sampling day covering a group of geographically close stations.

A set of sample documentation forms was generated for each site before each sample run. These forms included a Sample Submission Form and a Test Request Form, which contained site information, sample description, an automatically assigned sample number, and the requested laboratory and field tests. The forms were generated from a Field and Laboratory Information Management System (FLIMS), an automatic lab information, data tracking, and management system. Field staff also uses the FLIMS system to prepare sample containers and preservation methods. Bryte Chemical Laboratory of the Office of Water Quality supplied all necessary sampling materials to the Field Support unit and performed all the laboratory analyses included in this report. Bryte Laboratory's requirements for sample

containers, preservation techniques, and sample holding times for the included constituents are summarized in Table 2-1.

Samples were collected from each site approximately 3 feet below the surface. At stations with a sample collection platform, a stainless steel bucket was used to collect the sample. At stations without a platform, a round, 2-liter, stainless steel container attached to the end of a 15-foot extension pole was used to collect the sample; in this case, 4 or 5 subsamples were combined to make a composite sample.

All samples were prepared and filtered, when necessary, onsite in a specially equipped mobile laboratory van. Samples were preserved according to techniques listed in Table 2-1 and stored on ice inside an ice chest for transportation to Bryte Laboratory. Certain field measurements were also taken onsite, but these measurements are not included in this report. However, certain onsite measurements were useful during internal data audits when laboratory data for the same measurements seemed questionable. Large discrepancies between field and laboratory values occasionally triggered corrective action in the laboratory. Details about corrective actions made on data presented in this report are discussed in Chapter 9.

For quality control purposes, the Field Support unit regularly collects QA/QC samples according to U.S. Environmental Protection Agency QA/QC requirements. These samples often included equipment blanks, field blanks, and duplicate site samples. QA/QC samples were processed in the same manner as regular grab samples.

## **Laboratory Analysis**

Bryte Chemical Laboratory of DWR analyzed all samples for constituents presented in this report. Bryte Laboratory is a fully certified environmental laboratory in West Sacramento. The methods and reporting limits for the included constituents are summarized in Table 2-2.

Samples were submitted to the laboratory on the same day of collection. A Test Request Form specifying the requested analyses was submitted to the laboratory for each sample. The sample container was labeled with FLIMS-generated sample labels indicating the sample identification number and other required information. After the samples and necessary forms were cross-checked and verified, the receiving clerk at Bryte signed and dated the Test Request Forms with a copy to the sampler. All samples received by the laboratory were placed in appropriate storage cabinets for various sample types (that is, metals, standard minerals, etc.) or sent directly to the test area.

All pertinent field information—including date, time, location, sampling personnel, field measurements, requested laboratory tests, and additional information—was logged into and tracked by the FLIMS system after sample collection. Following data login, FLIMS notified laboratory personnel of the samples to be analyzed. The samples were then processed within an allowed holding time (Table 2-1). Analytical results were entered into FLIMS, which is connected to the DWR Water Data Library (WDL), the destination database for all Municipal Water Quality Investigations monitoring data.

Table 2-1 MWQI water sample collection and preservation

Table 2-2 Analytical methods and reporting limits for included constituents

## **Data Quality**

Once analyses were completed, the remaining sample was kept for 30 to 60 days in storage before being discarded. The storage time is necessary for evaluating and ensuring acceptable results. Bryte Laboratory follows a set of internal QA/QC audit procedures, which include evaluation of data for blanks (laboratory and field), calibration standards, laboratory control samples, etc. The detailed QA/QC procedures and corrective actions have been described in Bryte Laboratory's latest QA technical documentation (Fong 2002). The Quality Assurance/Quality Control unit of the Municipal Water Quality Program Branch, Office of Water Quality, performs data quality checks routinely on data in WDL. Results of data quality evaluations for constituents included in this report are presented in Chapter 9.

In this report, constituents testing below their reporting limits are treated as "non-detect" and are not included in the summary statistics (discussed below). During the reporting period, occasional method changes occurred for some constituents due to adoption of improved techniques, equipment failures, or staff limitations. Constituents that may be analyzed by more than one method are shown in Table 2-2. To minimize discrepancy of data resulting from method changes, this report included data from a single method for each constituent whenever possible. For some limited number of constituents, data from different methods had to be combined. When this occurred, the data from different methods were comparable based on the comparability guidelines (Agee 2002 pers comm). All data conversions and data from more than one method are documented throughout this report.

## **Statistical Analysis**

Statistical methods were used to show summary statistics. The focus of this report is to demonstrate the general status and trends of various constituents throughout the Delta; therefore, most data are presented using simple descriptive graphics with mostly simple summary statistics. More advanced statistical analyses were also performed to show temporal and spatial variations, constituent sources such as the effects of rice drainage and other agricultural activity on water quality at some Sacramento and San Joaquin River stations. Nonparametric statistical methods were used when parametric assumptions were not met. A statistical computing package, the SAS® System for Windows Version 8.2, was used for all statistical analyses. The SAS® System was developed and supported by SAS® Institute, Inc, Cary, NC.

### **Descriptive Plots**

Descriptive plots are mostly in the form of temporal graphs. Monthly or weekly data are plotted with time to demonstrate general behavior of the data during the reporting period. Data interpretation based on traditional bar charts or scatter plots are not always reliable. In this report, a new statistical regression method called the Loess Smooth Procedure was used for exploratory data analysis to demonstrate seasonal trends and to compare differences among sites.

Loess stands for local regression. It implements a nonparametric method for estimating local regression for situations where there is no suitable

parametric form of the regression model. The idea of local regression is that at a predictor level the regression function can be locally approximated by the value of a function in some specified parametric class and is obtained by fitting a regression line to the data points within a chosen neighborhood of a specific predictor level. Weighted least-squares is used to fit linear or quadratic functions of the predictors at the centers of neighborhoods. The radius of each neighborhood is chosen and is called the smoothing parameter. A detailed description of the procedure can be found in SAS/STAT User's Guide (SAS<sup>®</sup> Institute 1999).

One advantage of the Loess procedure is that when outliers are present the effect of these outliers on the overall regression is minimized and a robust fitting can be achieved because the overall regression is the result of local regression fittings to the centers of each individual neighborhood. The Loess smooth will not be helpful for very small data sets, but it is a useful tool for exploratory data analysis on large data sets.

The procedure is particularly useful for analysis of water quality data, which may contain outliers. No parametric regression is available for this type of water quality data. Data interpretation based on traditional bar or scatter plots are statistically unreliable. However, scatter plots smoothed by the Loess procedure provide a more statistically defensible, robust regression analysis, which provides insight into seasonal differences and demonstrates the influences of constituent sources during a given time period.

### **Descriptive Statistics**

This report used predominantly the following summary statistics:

- Data range: data between the minimum and the maximum.
- Majority data range: data between the 5th and 95th percentiles.
- Interquartile range (IQR): data range between the 25th and the 75th percentile. The IQR is preferred over the standard deviation because it is the most commonly used resistant measure of data spread and dispersion. It measures the range of the central 50% of the data, and is not influenced at all by the 25% of the data on either end (Helsel and Hirsch 1992). The wider the IQR, the greater the dispersion of the majority of the data.
- Mean: presented mostly for historical reasons. Skewed data of wide variability such as water quality data should not be averaged because the mean is usually strongly influenced by data at both ends and is often misleading.
- Median: more resistant measure for water quality data, thus a preferred measure over the mean. When adequate this report uses the median to represent baseline levels of water quality constituents.

### **Nonparametric Statistical Methods**

The majority of monitoring data for the included constituents was not normally distributed, thus parametric statistical methods may not be robust. In this report, 2 nonparametric tests—the Wilcoxon Rank-sum Test and the Kruskal Wallis Test—were used for comparisons among stations. These nonparametric tests are as powerful as their parametric equivalents but do not require normal data distribution.

Table 2-1 MWQI water sample collection and preservation

Determination	Container	Sample preparation	Sample size (mL)	Preservative	Holding time
Alkalinity	Polyethylene	Filtered	500	4 °C	14 days
Electrical conductivity (EC)	Polyethylene	Filtered	500	4 °C	28 days
Haloacetic acid (HAA)	Glass, amber VOA	Unfiltered	40, X 2, Teflon, no air	4 °C	7d ext, 21d after ext
Haloacetic acid formation potential (HAAFP)	Glass, amber VOA	Filtered	40, X 3, Teflon, no air	4 °C	7d ext, 21d after ext
Hardness by calculation	Polyethylene	Filtered	250	HNO <sub>3</sub> , pH<2	6 months
Hardness, total by calculation	Polyethylene	Unfiltered	250	HNO <sub>3</sub> , pH<2	6 months
ICP cations, dissolved - Na,Ca,Mg, K, B, Si	Polyethylene, acid washed	Filtered	250	HNO <sub>3</sub> , pH<2	6 months
ICP cations, total - Na,Ca,Mg, K, B, Si	Polyethylene, acid washed	Unfiltered	250	HNO <sub>3</sub> , pH<2	6 months
ICP/MS trace metals, dissolved	Polyethylene, acid washed	Filtered	500	HNO <sub>3</sub> , pH<2	6 Months
ICP/MS trace metals, total	Polyethylene, acid washed	Unfiltered	500	HNO <sub>3</sub> , pH<2	6 Months
IC anions - CI, SO <sub>4</sub> , Br, F	Polyethylene	Filtered	500	4 °C	28 days
Mercury by cold vapor	Polyethylene, acid washed	Unfiltered	500	4 °C, HNO <sub>3</sub> , pH<2	28 days
Mercury by ICP/MS	Polyethylene, acid washed	Filtered	500	4 °C, HNO <sub>3</sub> , pH<2	28 days
Nitrate, nitrite (nutrient)	Polyethylene	Filtered	250	-20 °C, dark	48 hours
Nitrate, nitrite (nutrient DWR Modified)	Polyethylene	Filtered	250	-20 °C, dark	28 days
Nitrate, nitrite (Std Mineral-IC Anions)	Polyethylene	Filtered	500	4 °C	48 hours
Nitrate, nitrite (Std Mineral DWR Modified)	Polyethylene	Filtered	500	4 °C	28 days
Nitrogen, ammonia	Polyethylene	Filtered	250	-20 °C, dark	28 days
Nitrogen Kjeldahl, total (TKN)	Polyethylene	Unfiltered	250	-20 °C, dark	28 days
Organic carbon, dissolved (DOC)	Glass, clear VOA	Filtered	40	4 °C, HNO <sub>3</sub> , pH<2	28 days
Organic carbon, total (TOC)	Glass, clear VOA	Unfiltered	40	4 °C, HNO <sub>3</sub> , pH<2	28 days
Orthophosphate	Polyethylene	Filtered	250	4 °C	48 hours
Orthophosphate DWR modified	Polyethylene	Filtered	250	-20 °C, dark	28 days
рН	Polyethylene	Unfiltered	250	4 °C	ASAP

Table continued on next page

Table 2-1 continued

Determination	Container	Sample preparation	Sample size (mL)	Preservative	Holding time
Phosphorous, total	Polyethylene	Unfiltered	250	-20 °C, dark	28 days
Solids, total dissolved (TDS)	Polyethylene	Filtered	500	4 °C	7 days
Trihalomethane (THM)	Glass, amber VOA	Unfiltered	40, X 2, Teflon, no air	4 °C, HCl, pH<2	14 days
Trihalomethane formation potential (THMFP)	Glass, amber VOA	Filtered	40, X 3, Teflon, no air	4 °C	7 days after chlorination
Turbidity	Polyethylene	Unfiltered	500	4 °C	48 hours
UVA	Polyethylene	Filtered	250	4 °C	14 days
Volatile organic analysis (MTBE, etc.)	Glass, amber VOA	Unfiltered	40, X 2, Teflon, no air	4 °C, HCl, pH<2	14 days

Note: Condensed from Appendix A, *Bryte Chemical Laboratory Quality Assurance Manual* (Fong 2002). ext = extraction

Table 2-2 Analytical methods and reporting limits for included constituents

Constituent	Method source	Method number	Reporting limit <sup>a</sup>
Total organic carbon (TOC)	Std methods	5310 D, Wet oxidation, IR, automated	0.1
	EPA	415.1 Wet oxidation, IR, automated	0.1
Dissolved organic carbon (DOC)	EPA	415.1 Wet oxidation, IR, automated	0.1
Trihalomethane formation potential (THMFP)	EPA	510.1 (modified) GC, purge and trap	1
Haloacetic acids		552.2 Gas chromatography (GC)	1
UV absorbance at 254 nm	Std methods	5910 B UV-absorbing organics	0.001 cm <sup>-1</sup>
MTBE	EPA	502.2 purge and trap	0.5
Bromide		300.0 ion chromatography	0.01
Electrical conductivity	Std methods	2310 B Wheatstone Bridge	1 μS/cm
	EPA	120.1 Wheatstone Bridge	1 μS/cm
Total dissolved solids (TDS)	Std methods	2540 C Gravimetric, dried at 180° C	1
	EPA	160.1 Gravimetric, dried at 180° C	1
Chloride	Std methods	4500-CI-E Colorimetric, Ferricyanide	1
Sulfate		375.2 Colorimetric, Methythymol Blue	1
		300.0 Ion Chromatography	1
Calcium	EPA	215.1 AA Flame	1
		200.7 ICP	1
Magnesium		242.1 AA Flame	1
		200.7 ICP	1
Sodium		273.1 AA Flame	1
		200.7 ICP	1
рН	Std methods	4500 H <sup>+</sup> Electrometric	0.1 pH unit
	EPA	150.1 Electrometric	0.1 pH unit
Alkalinity	Std methods	2320 B Titrimetric	1
	EPA	310.1 Titrimetric	1
Hardness	Std methods	2340 B total by calculation	
Turbidity		2130 B Nephelometric	1 NTU
	EPA	180.1 Nephelometric	1 NTU

a. Unit is mg/L unless otherwise indicated.

Table 2-2 continued

Constituent	Method source	Method number	Reporting limit <sup>a</sup>
Aluminum	EPA	200.7 ICP	0.05
		200.8 ICP/MS	0.01
		200.9 GFAA	0.01
Antimony	EPA	200.7 ICP	0.025
		200.8 ICP/MS	0.001
Arsenic	Std methods	3114, AA gaseous hybride	0.001
	EPA	200.7 ICP	0.05
		200.8 ICP/MS	0.001
Barium	EPA	200.7 ICP	0.01
		200.8 ICP/MS	0.05
		200.9 GFAA	0.05
		208.2 GFAA	0.05
Boron	USGS	I-2115-85 Colorimetric, Azomethine	0.1
Cadmium	EPA	200.7 ICP	0.01
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		213.2 GFAA	0.005
Total chromium (all valencies)	EPA	200.7 ICP	0.02
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		218.2 GFAA	0.005
Cobalt	EPA	200.7 ICP	0.02
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		219.2 GFAA	0.005
Copper	EPA	200.7 ICP	0.02
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		220.1 AA Flame	0.1
		220.2 GFAA	0.005

a. Unit is mg/L unless otherwise indicated.

Table 2-2 continued

Constituent	Method source	Method number	Reporting limit <sup>a</sup>
Iron	EPA	200.7 ICP	0.025
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		236.1 AA Flame	0.1
		236.2 GFAA	0.005
Lead	EPA	200.7 ICP	0.05
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		239.2 GFAA	0.005
Manganese	EPA	200.7 ICP	0.01
		200.9 GFAA	0.005
		243.1 AA Flame	0.1
		243.2 GFAA	0.005
Mercury	EPA	245.1 AA, Flameless, cold vapor	0.001
Molybdenum	EPA	200.7 ICP	0.02
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		246.2 GFAA	0.005
Nickel	EPA	200.7 ICP	0.025
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		249.1 AA Flame	0.1
		249.2 GFAA	0.005
Selenium	Std Methods	3114B AA gaseous hydride	0.001
	EPA	200.8 ICP/MS	0.001
Silver	EPA	200.7 ICP	0.025
		200.8 ICP/MS	0.001
		200.9 GFAA	0.005
		272.2 GFAA	0.005

a. Unit is mg/L unless otherwise indicated.

Table continued on next page

Table 2-2 continued

Constituent	Method source	Method number	Reporting limit <sup>a</sup>
Zinc	EPA	200.7 ICP	0.02
		200.8 ICP/MS	0.005
		200.9 GFAA	0.005
		289.1 AA Flame, Direct	0.1
		289.2 GFAA	0.005
Ammonia	Std methods	4500-NH <sub>3</sub> B, G Automated Phenate	0.01
	EPA	350.1 Automated Phenate	0.01
Total Kjeldahl nitrogen	EPA	351.2 Colorimetric, semi-automated	0.1
Nitrate	Std methods	4500-NO <sub>3</sub> -F Cd-Reduction	0.01
	EPA	353.2 Cd-Reduction, Automated	0.01
Nitrite + nitrate	EPA	353.2, Cd-Reduction, Automated	0.01
Orthophosphate	Std methods	4500-P-E Colorimetric, Ascorbic Acid	0.01
	EPA	365.1 Colorimetric, Ascorbic Acid	0.01
Phosphorus, total	EPA	365.4 Colorimetric, semi-automated	0.01

Note: Condensed from Appendix G, *Bryte Chemical Laboratory Quality Assurance Manual* (Fong 2002).

a. Unit is mg/L unless otherwise indicated.